

Ground state properties of heavy alkali halides

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We extend previous work on alkali halides by calculations for the heavy-atom species RbF, RbCl, LiBr, NaBr, KBr, RbBr, LiI, NaI, KI, and RbI. Relativistic effects are included by means of energy-consistent pseudopotentials, correlations are treated at the coupled-cluster level. A striking deficiency of the Hartree-Fock approach are lattice constants deviating by up to 7.5 % from experimental values which is reduced to a maximum error of 2.4 % by taking into account electron correlation. Besides, we provide *ab-initio* data for in-crystal polarizabilities and van der Waals coefficients.

Calculations for solids based on the *exact* Hartree-Fock (HF) exchange have been widely used for determining total energies, lattice constants, elastic properties, phase transitions, equations of state, and also magnetic properties^{1,2}. In Ref. 3, it was shown how a correlation treatment with quantum-chemical methods could be performed for semiconductors. We extended this to ionic systems⁴ and recently presented results for six light alkali halide systems⁵; we now turn to their heavier counterparts, where correlation effects are stronger and relativistic effects should be included. We restrict ourselves to a comparison of different systems with NaCl structure. The method has been explained in Ref. 5.

I. HARTREE-FOCK CALCULATION

We performed self-consistent-field (SCF) calculations with the program package CRYSTAL 95 (Ref. 6). For Li, Na, K, F and Cl, we used the basis sets given in Ref. 7. The most diffuse *sp*-exponents were reoptimized (Table I). For the free metal atoms one more diffuse *sp* shell was added (*sp*-exponents are 0.048 for Li, 0.040 for Na, and 0.028 for K). For Rb, Br, and I, we used relativistic pseudopotentials (for details cf. section II) in combination with the corresponding basis sets, again reoptimizing diffuse exponents (Table I). For Rb, the first three *s* and *p* exponents were kept contracted from the atom-optimized basis set, and two *sp* exponents optimized in calculations for the solid were added, yielding a [3s3p] basis set after these steps. For Br and I, the two tight atomic *s* and *p* exponents were kept fixed, and two diffuse *s* and *p* exponents were optimized which resulted in a [4s4p] basis set. We optimized one *d* function for the

heavier alkali metal ions (Table I). This leads to a tiny increase of the cohesive energy and a reduction of the bond length of $\lesssim 0.5\%$. Adding *d*-functions to the anions virtually does not change the results (see also Ref. 7). Cohesive energies with respect to neutral atoms are strongly underestimated at the SCF level, by up to 29%. Lattice constants are too large by up to 7.5 % and, as a consequence, bulk moduli are underestimated by up to 36% (see also earlier calculations^{8,2}).

II. CORRELATION CALCULATION

We performed correlation calculations using the coupled cluster approach with single and double substitutions (CCSD) and with the inclusion of triples within the framework of perturbation theory (CCSD(T)⁹) using the program package MOLPRO^{10,11}. For Li, Na, K, F, and Cl, we used the same basis sets as in Ref. 5. For Rb, we applied the scalar-relativistic energy-consistent small-core (9-valence-electron) pseudopotential¹² together with the corresponding atom-optimized basis set (uncontracted), and augmented the latter with 5 *d* functions and 3 *f* functions, resulting in a [7s6p5d3f] basis set (*d* exponents are 0.801 900, 0.297 000, 0.110 000, 0.040 741, 0.015 089, *f* exponents are 1.320 000, 0.600 000, 0.272 727). For Br and I, 7-valence-electron pseudopotentials, again of the scalar-relativistic energy-consistent variety, were used¹³. *s* and *p* functions were left uncontracted, three *d* and two *f* functions were added, so that the final basis sets are [4s5p3d2f] (Br *d* exponents are 0.604 185, 0.271 744, and 0.095, *f* exponents are 0.58 and 0.26; I *d* exponents are 0.367 696, 0.183 848, and 0.07, *f* exponents are 0.43 and 0.19).

In Table II, we show atomic ionization potentials (IP) and electron affinities (EA). The correlation contribution to the EA decreases from F to I with increasing size of the atoms: the additional electron completes the shell and correlations are more important in shells with smaller radii. In the metal atoms, the correlation contribution to the IP (or the EA of the corresponding cations) increases from Li to Rb. The additional electron is the only electron in the open shell and the main correlation effect is a dynamical core polarization. The correlation energy is $-\frac{1}{2}\alpha\vec{E}^2$ (α is the core polarizability, \vec{E} is the instantaneous field of the valence electron at the site of the core¹⁴). The higher polarizabilities of the heavier ions lead to larger absolute correlation energies.

III. RESULTS FOR THE SOLID AND DISCUSSION

In the solid, the correlation energies of the cations are nearly the same as for free ions. The correlation energies of the diffuse anions become significantly smaller in magnitude (cf. Tables III,IV,V). This originates from the upward energy shift of excited-state determinants when the anions are compressed. The difference in correlation energies $|\epsilon_{corr}(\text{free anion}) - \epsilon_{corr}(\text{embedded anion})|$ decreases from F to I: since the size of the valence shell is smaller for atoms with low main quantum number, the concomitant correlation energy is larger and the compression due to the neighboring ions leads to a stronger change of the correlation energy.

Two-body contributions are shown in Tables III,IV,V. Their magnitude is essentially determined by the distance and the polarizabilities. We evaluated two-body increments typically up to third nearest neighbors for halide-halide and metal-halide pairs, metal-metal increments for nearest neighbors only. We used the two-body increments for next neighbors to calculate van der Waals C_6 coefficients ($E_{vdW} = -\frac{C_6}{r^6}$). Polarizabilities increase with increasing atomic radii and electron number from Li to Rb and from F to I, but are roughly constant for the same ion in different halides (cf. Table VI). Evaluating London's formula gives a qualitative explanation of the relative strength of the van der Waals interaction in different systems.

Including electron correlation with CCSD(T), we obtain nice agreement with experiment with a deviation of 7 % for cohesive energies or 5% for lattice energies in the worst case (Table VII). For lattice constants, the remaining largest deviation from experiment at the CCSD(T) level is 2.4 %. Bulk moduli are consistently in better agreement with experiment after including correlations, at the CCSD(T) level the maximum deviation is 15 % or 6 % on average. We are aware of one density functional calculation for these systems¹⁵. Although the local density approximation was applied, i.e. no gradient correction, the agreement with experiment is not worse than with our approach. Still, our approach has the advantage of being free of parameters and calculation of EAs or IPs does not pose problems. Moreover, a detailed interpretation of correlation effects is possible. However, for calculating the correlation energy at one lattice constant, $\lesssim 10$ hours of CPU time on workstations are necessary (when three-body corrections are neglected which are the most expensive ones), whereas a density functional calculation will be much faster (analogously, the CRYSTAL-SCF calculation takes only a few minutes).

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TABLE I. Diffuse exponents of Gaussian basis sets, and polarization functions, for the CRYSTAL calculations

System	cation	anion
RbF	<i>sp</i> 0.336, 0.136, <i>d</i> 0.38	<i>sp</i> 0.429, 0.133
RbCl	<i>sp</i> 0.334, 0.140, <i>d</i> 0.30	<i>sp</i> 0.322, 0.114, <i>d</i> 0.50
LiBr	<i>sp</i> 0.513	<i>s</i> 0.400, 0.145, <i>p</i> 0.324, 0.107
NaBr	<i>sp</i> 0.538, 0.198	<i>s</i> 0.389, 0.141, <i>p</i> 0.315, 0.107
KBr	<i>sp</i> 0.394, 0.219, <i>d</i> 0.42	<i>s</i> 0.392, 0.140, <i>p</i> 0.326, 0.108
RbBr	<i>sp</i> 0.336, 0.141, <i>d</i> 0.31	<i>s</i> 0.393, 0.140, <i>p</i> 0.323, 0.105
LiI	<i>sp</i> 0.511	<i>s</i> 0.327, 0.122, <i>p</i> 0.322, 0.101
NaI	<i>sp</i> 0.533, 0.176	<i>s</i> 0.323, 0.124, <i>p</i> 0.321, 0.104
KI	<i>sp</i> 0.397, 0.219, <i>d</i> 0.45	<i>s</i> 0.324, 0.121, <i>p</i> 0.321, 0.101
RbI	<i>sp</i> 0.333, 0.141, <i>d</i> 0.31	<i>s</i> 0.322, 0.120, <i>p</i> 0.322, 0.099

 TABLE II. Electron affinities (EA) for halogen atoms and ionization potentials (IP) for alkali atoms, in Hartree units. The second column gives the value for EA or IP at the Hartree-Fock level, the fourth and sixth at correlated levels. The third and fifth column provide separate correlation contributions to EA and IP at CCSD and CCSD(T) level, respectively. Finally, the last column shows the experimental values. Since our calculated values for the neutral halogen atoms are without spin-orbit coupling, i.e. averaged over the $^3P_{1/2}$ and $^3P_{3/2}$ states, we give in brackets experimental results after averaging over these two states.

System	HF=EA/IP (HF)	CCSD	EA/IP (CCSD)	CCSD(T)	EA/IP (CCSD(T))	exp. EA/IP ^{16,17}
F \rightarrow F ⁻	0.050704	0.065415	0.116119	0.071218	0.121922	0.12499 (0.12560)
Cl \rightarrow Cl ⁻	0.095053	0.030997	0.126051	0.034132	0.129186	0.13276 (0.13410)
Br \rightarrow Br ⁻	0.093216	0.026662	0.119877	0.029237	0.122452	0.12361 (0.12921)
I \rightarrow I ⁻	0.092016	0.021998	0.114014	0.024216	0.116232	0.11242 (0.12397)
Li \rightarrow Li ⁺	0.196311	0.000994	0.197305	0.001023	0.197334	0.19814
Na \rightarrow Na ⁺	0.181948	0.005904	0.187852	0.006156	0.188104	0.18886
K \rightarrow K ⁺	0.146785	0.009586	0.156371	0.010446	0.157231	0.15952
Rb \rightarrow Rb ⁺	0.139571	0.011481	0.151052	0.012392	0.151963	0.15351

TABLE III. Local correlation energies per primitive unit cell (in Hartree) for RbF (at a lattice constant of 5.65 Å) and RbCl (6.65 Å)

	RbF		RbCl	
	CCSD	CCSD(T)	CCSD	CCSD(T)
free Rb ⁺ \rightarrow embedded Rb ⁺	-0.000015	-0.000018	-0.000005	-0.000006
free X ⁻ \rightarrow embedded X ⁻	+0.010103	+0.012906	+0.002433	+0.003435
sum of X-X increments	-0.000753	-0.000879	-0.002465	-0.002915
sum of Rb-X increments	-0.016480	-0.018827	-0.016480	-0.018736
sum of Rb-Rb increments	-0.002718	-0.003021	-0.000802	-0.000893
total sum	-0.009863	-0.009839	-0.017319	-0.019115

TABLE IV. Local correlation energies per primitive unit cell (in Hartree) for LiBr (at a lattice constant of 5.50 Å), NaBr (5.98 Å), KBr (6.70 Å), and RbBr (7.00 Å).

	LiBr		NaBr		KBr		RbBr	
	CCSD	CCSD(T)	CCSD	CCSD(T)	CCSD	CCSD(T)	CCSD	CCSD(T)
free $M^+ \rightarrow$ embedded M^+	-0.000011	-0.000011	-0.000086	-0.000093	-0.000003	-0.000004	-0.000004	-0.000004
free $Br^- \rightarrow$ embedded Br^-	+0.001802	+0.002489	+0.001778	+0.002455	+0.001682	+0.002353	+0.001716	+0.002422
sum of Br-Br increments	-0.015871	-0.018428	-0.009360	-0.010917	-0.004218	-0.004933	-0.002957	-0.003452
sum of M-Br increments	-0.002429	-0.002599	-0.006814	-0.007449	-0.013715	-0.015675	-0.015936	-0.018034
sum of M-M increments	absolute value $<10^{-6}$		-0.000037	-0.000040	-0.000283	-0.000320	-0.000569	-0.000633
total sum	-0.016509	-0.018549	-0.014519	-0.016044	-0.016537	-0.018579	-0.017750	-0.019701

TABLE V. Local correlation energies per primitive unit cell (in Hartree) for LiI (at a lattice constant of 6.05 Å), NaI (6.50 Å), KI (7.20 Å), and RbI (7.45 Å).

	LiI		NaI		KI		RbI	
	CCSD	CCSD(T)	CCSD	CCSD(T)	CCSD	CCSD(T)	CCSD	CCSD(T)
free $M^+ \rightarrow$ embedded M^+	-0.000007	-0.000007	-0.000070	-0.000076	-0.000002	-0.000003	-0.000002	-0.000003
free $I^- \rightarrow$ embedded I^-	+0.001007	+0.001470	+0.001038	+0.001503	+0.001031	+0.001508	+0.001088	+0.001604
sum of I-I increments	-0.018703	-0.021757	-0.011833	-0.013815	-0.005666	-0.006632	-0.004139	-0.004835
sum of M-I increments	-0.002153	-0.002304	-0.006200	-0.006776	-0.012961	-0.014807	-0.015830	-0.017900
sum of M-M increments	absolute value $<10^{-6}$		-0.000022	-0.000024	-0.000178	-0.000202	-0.000377	-0.000420
total sum	-0.019856	-0.022598	-0.017087	-0.019188	-0.017776	-0.020136	-0.019260	-0.021554

TABLE VI. Comparison of CCSD two-body increments ΔE between next neighbors (weight factors for the solid not included). All results are given in atomic units (except for the lattice constant in column 2). r is the distance between the respective ions in bohr. IP_{cat} and IP_{an} are in-crystal ionization potentials for the respective ions, α_{cat} and α_{an} the corresponding polarizabilities. In the last column, results from CCSD calculations are divided by those obtained from a simple estimate using the London formula.

System	lattice constant a in Å	ΔE	$-C_6 = \Delta E \times r^6$	IP_{cat}	IP_{an}	α_{cat}	α_{an}	$-\frac{2}{3} \frac{r^6}{\alpha_1 \alpha_2} \frac{IP_1 + IP_2}{IP_1 IP_2} \times \Delta E$
Li-Li (LiF)	3.99	~ -0.000003	~ -0.07	2.3		0.19		~ 1.1
F-F (RbF)	5.65	-0.000111	-20.6	0.67	0.40	8.9	5.1	2.6
Rb-F (RbF)	5.65	-0.002625	-60.8					3.6
Rb-Rb (RbF)	5.65	-0.000411	-76.1					1.9
Cl-Cl (RbCl)	6.65	-0.000370	-182	0.72	0.37	8.9	17.8	2.1
Rb-Cl (RbCl)	6.65	-0.002626	-162					2.8
Rb-Rb (RbCl)	6.65	-0.000134	-66.0					1.5
Br-Br (LiBr)	5.50	-0.002423	-382	2.4	0.43	0.19	23.1	2.2
Li-Br (LiBr)	5.50	-0.000405	-7.98					3.3
Br-Br (NaBr)	5.98	-0.001431	-373	1.4	0.40	0.97	23.3	2.3
Na-Br (NaBr)	5.98	-0.001090	-35.5					3.4
Na-Na (NaBr)	5.98	-0.000006	-1.56					1.6
Br-Br (KBr)	6.70	-0.000641	-330	0.87	0.37	5.4	23.1	2.2
K-Br (KBr)	6.70	-0.002193	-141					2.9
K-K (KBr)	6.70	-0.000047	-24.2					1.3
Br-Br (RbBr)	7.00	-0.000447	-299	0.74	0.36	8.9	22.4	2.2
Rb-Br (RbBr)	7.00	-0.002545	-213					-2.9
Rb-Rb (RbBr)	7.00	-0.000095	-63.6					1.4
I-I (LiI)	6.05	-0.002863	-799	2.4	0.40	0.19	35.0	2.2
Li-I (LiI)	6.05	-0.000359	-12.5					3.7
I-I (NaI)	6.50	-0.001814	-779	1.4	0.37	0.97	35.0	2.3
Na-I (NaI)	6.50	-0.000995	-53.4					3.6
Na-Na (NaI)	6.50	~ -0.000004	~ -1.72					~ 1.7
I-I (KI)	7.20	-0.000865	-686	0.89	0.35	5.4	34.4	2.2
K-I (KI)	7.20	-0.002078	-206					2.9
K-K (KI)	7.20	-0.000030	-23.8					1.2
I-I (RbI)	7.45	-0.000630	-613	0.75	0.33	8.9	32.7	2.3
Rb-I (RbI)	7.45	-0.002535	-308					3.1
Rb-Rb (RbI)	7.45	-0.000063	-61.3					1.4

TABLE VII. Hartree-Fock (HF) and correlated results (CCSD, CCSD(T)), in comparison to density-functional (DFT) and experimental values, for the solids. Cohesive energies E (with respect to neutral atoms) and lattice energies E_{lat} (with respect to free ions) are given in Hartree units (taken from Ref. 16), lattice constants a in Å (Ref. 18) and bulk moduli B in GPa. Zero point energies have been estimated with a Debye approximation (Debye temperatures taken from Ref. 19) and added to the experimental cohesive energies. Results for experimental cohesive energies averaged over $^3P_{1/2}$ and $^3P_{3/2}$ states of the neutral halogen atoms are given in brackets. The experimental bulk moduli are at 4.2 K and have been taken from Ref. 15 and references therein, except for KBr and LiI where data from Refs. 20 and 21, respectively, have been extrapolated to zero temperature with the temperature dependence taken from these references.

	HF	CCSD	CCSD(T)	DFT (Ref. 15)	expt.
RbF					
E_{lat}	0.2839	0.2925	0.2925		0.304
E	0.1946	0.2572	0.2620	0.279	0.276 (0.277)
a	5.819	5.671	5.657	5.73	5.588
B	24.9	31.1	31.5	26.1	30.1
RbCl					
E_{lat}	0.2407	0.2561	0.2579		0.265
E	0.1963	0.2312	0.2352	0.232	0.244 (0.245)
a	6.912	6.659	6.635	6.57	6.532
B	13.4	17.4	18.2	16.6	18.7
LiBr					
E_{lat}	0.2863	0.3014	0.3034		0.315
E	0.1852	0.2260	0.2306	0.235	0.240 (0.246)
a	5.690	5.512	5.492	5.44	5.459
B	24.6	27.5	27.5	28.5	26.3
NaBr					
E_{lat}	0.2656	0.2790	0.2805		0.288
E	0.1777	0.2118	0.2156	0.206	0.223 (0.229)
a	6.181	5.984	5.966	6.10	5.926
B	15.4	21.6	22.2	18.6	22.6
KBr					
E_{lat}	0.2353	0.2504	0.2525		0.264
E	0.1849	0.2170	0.2208	0.220	0.228 (0.234)
a	6.939	6.685	6.654	6.57	6.541
B	12.6	16.0	16.4	16.3	17.9
RbBr					
E_{lat}	0.2274	0.2434	0.2454		0.255
E	0.1812	0.2123	0.2160	0.213	0.225 (0.231)
a	7.269	6.996	6.967	6.87	6.822
B	10.8	14.8	15.0	14.1	16.0
LiI					
E_{lat}	0.2594	0.2775	0.2803		0.293
E	0.1572	0.1962	0.2012	0.202	0.207 (0.219)
a	6.299	6.034	6.002	5.91	5.946
B	15.3	20.5	21.6	22.0	24.0
NaI					
E_{lat}	0.2443	0.2596	0.2616		0.269
E	0.1551	0.1865	0.1906	0.173	0.193 (0.205)
a	6.756	6.525	6.499	6.58	6.409
B	13.7	18.1	18.6	14.9	17.9
KI					
E_{lat}	0.2181	0.2342	0.2366		0.248
E	0.1665	0.1949	0.1987	0.191	0.201 (0.213)
a	7.473	7.182	7.143	7.01	6.994
B	10.5	12.9	13.1	13.8	12.7
RbI					
E_{lat}	0.2116	0.2283	0.2306		0.241
E	0.1642	0.1914	0.1950	0.187	0.200 (0.212)
a	7.805	7.476	7.436	7.31	7.263
B	8.6	11.0	11.2	12.2	13.1